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Unit Cell Parameters of a Pozzolan Reaction Product¹

GEORGE R. GLENN AND R. L. HANDY²

Abstract. Powder X-ray analysis of a slurry of the dolomitic lime $\text{Ca}(\text{OH})_2 + \text{MgO}$ plus Otay bentonite, after being sealed and stored at room temperature for one year, showed complete loss of $\text{Ca}(\text{OH})_2$ and partial loss of the MgO , some or all of which went to $\text{Mg}(\text{OH})_2$. New X-ray lines indicate formation of pozzolan reaction products. Crystals of one of these products were isolated and studied by means of a diffractometer and single crystal orienter, and the unit cell was calculated. Individual crystals were then crushed to give Debye-Scherrer powder diffraction data. The chemical composition of the crystals is not yet known. Differential thermal and X-ray analysis of the reacted lime-bentonite mixture shows considerable alteration of the bentonite.

INTRODUCTION

Use of lime in roads dates back to Roman times, when lime mortar was used in the Appian Way. Early mortars were sand-lime, but after 150 B.C. the Romans also added a volcanic ash from near Pozzuoli, Italy, because this silicious glass seemed to improve cementing properties. Now any cementing reaction between lime and silicious materials is referred as a pozzolan reaction.

The nature of pozzolan reactions has been investigated only recently. Leonard and Davidson (1) report new X-ray diffraction peaks at 12.6 Å and 3.08 Å after reacting $\text{Ca}(\text{OH})_2$ and fly ash in a slurry for one year at room temperature, and report no peaks for mixes cured at 40°, 60°, and 80°C. They conclude from lime depletion data that the initial product in either case is non-crystalline, after which there is slow crystallization to calcium silicate hydrate I, similar to the mineral tobermorite. Tobermorite exists as 14, 11, 10 and 9 Å hydrates, and probably also as a 12.5 Å hydrate (2).

Minnick (3) reports new diffraction peaks at 3.31 Å, 3.05 Å, 2.97 Å, and 2.77 Å for $\text{Ca}(\text{OH})_2$ -fly ash samples either cured at 140°C or autoclaved, and essentially the same peaks with

¹ Contribution of the Iowa Engineering Experiment Station, Iowa State University, under the sponsorship of the Iowa Highway Research Board Project HR-48 with funds from the Iowa State Highway Commission. Special thanks are due to Capt. Jerry Ruff, U. S. Army Corps of Engineers, for loaning use of cured samples for the investigation, and to Dr. Donald Biggs, Dept. of Geology, Iowa State University, for helpful advice on use of the universal stage in determining optical properties.

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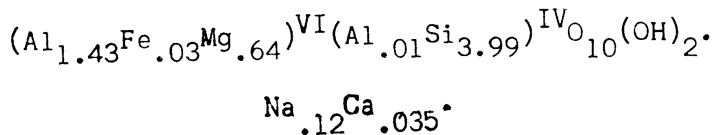
dolomitic lime, $\text{Ca}(\text{OH})_2 + \text{MgO}$. Minnick also notes that the MgO goes to $\text{Mg}(\text{OH})_2$.

It is now known that natural clay minerals react pozzolanically. Eades and Grim (4) report new diffraction lines for $\text{Ca}(\text{OH})_2$ -kaolinite cured at 60°C , the lines being at 5.09, 3.04, 2.8, and 1.8 Å. No new lines were found for lime-illite or lime-montmorillonite cured at the same temperature. Hilt and Davidson (5) report new diffraction lines at 8.11 and 7.59 Å for $\text{Ca}(\text{OH})_2$ -Montmorillonite reacted for 30 days at room temperature. The 7.59 Å compound was isolated and found to be rhombohedral, with lattice constants in the hexagonal system, $a_0 = 5.7550$ Å and $C_0 = 46.654$ Å. The compound was tentatively identified as a hydrated calcium aluminate. Despite its sharpness, an additional 8.11 Å peak was assigned to montmorillonite.

In the closely allied field of Portland cement chemistry, hydration of tricalcium silicate six days at room temperature in a ball mill (6) resulted in a product identified as the calcium silicate hydrate, afwillite, $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$, with a faint suggestion of tobermorite, with the same formula. The strong afwillite lines are at 6.61, 3.18, 2.83 (strongest), and 2.73 Å. Hydration for 21 to 30 months in a paste gave only poorly crystallized 11 Å hydrate tobermorite, with a very broad line at 3.03 Å and weaker lines at 11, 2.83, and 1.82 Å. Hydration of tricalcium aluminate results in a variety of metastable and stable hexagonal or cubic forms (7).

INVESTIGATION

Some investigators have found monohydrate dolomitic lime, $\text{Ca}(\text{OH})_2 + \text{MgO}$, to react more effectively with some soils than either high calcium lime, $\text{Ca}(\text{OH})_2$, or dolomitic lime with magnesium occurring as the hydroxide (8). The present study was initiated to attempt to characterize lime-clay pozzolanic reaction products by means of single crystal X-ray diffraction methods. As a first step a monohydrate dolomitic lime-montmorillonite-water mixture cured one year at room temperature was studied. The montmorillonite is Otay, California, bentonite, Reference Clay Mineral 24 (9), with the formula



The study mixture was a slurry of 40 gm of bentonite, 18 gm of lime, and 65 ml of distilled water. Mixed and sealed in a plastic cup, the mixture aged in a 100% humidity room for one year.

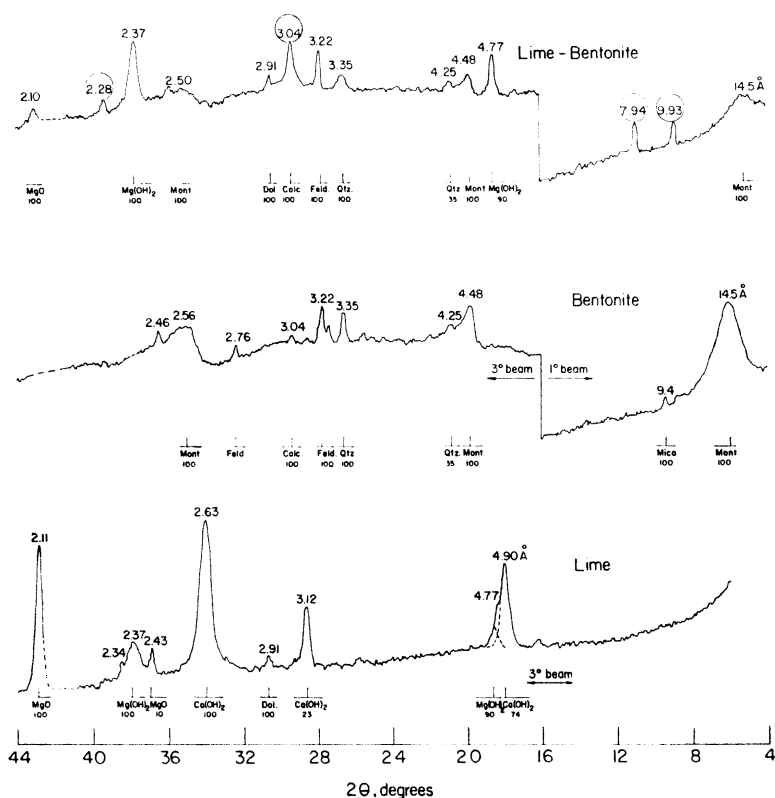


Figure 1. X-ray diffractometer traces for lime-bentonite after one year (top), unreacted bentonite alone (middle) and unreacted lime alone (bottom). Numbers above the peaks indicate Angstrom spacings; numbers below the identifications are A. S. T. M. Data File relative intensities for each component. New peaks are circled.

POWDER DATA FROM MIXTURE

Copper radiation X-ray diffractometer traces for powdered bentonite, lime, and lime-bentonite after one year were determined (figure 1). In the cured mixture there are no $\text{Ca}(\text{OH})_2$ peaks, and the MgO peaks are much diminished, indicating almost complete utilization of the lime. The montmorillonite peaks are much reduced, the quartz peaks appear reduced, but the feldspar peaks remain about the same. New products formed include $\text{Mg}(\text{OH})_2$, CaCO_3 , and unknown crystals giving peaks at 9.93, 7.94 and 2.28 Å. The 9.93 Å peak could be the 10 Å hydrate of tobermorite. Other strong peaks for this compound should be at 3.05 and 2.80 Å; the last does not appear. The strong 7.94 Å spacing does not coincide with any data known to the authors.

DIFFERENTIAL THERMAL ANALYSIS

D.T.A. of the raw bentonite gives characteristic endotherms

at 180°C, indicating loss of absorbed water, and 680°C, loss of OH's from the clay mineral structure. These are followed by an exotherm at 950°C indicating crystallization of new high-temperature phases. D.T.A. of lime shows a strong endotherm at 540°C for dehydration of $\text{Ca}(\text{OH})_2$, and at 370°C for dehydration of $\text{Mg}(\text{OH})_2$.

After pozzolanic reaction, the D.T.A. curve of the aged lime-bentonite mixture shows pronounced differences (figure 2).

A small montmorillonite endotherm remains at 680°. The small endotherm at 790° is assigned to calcite.

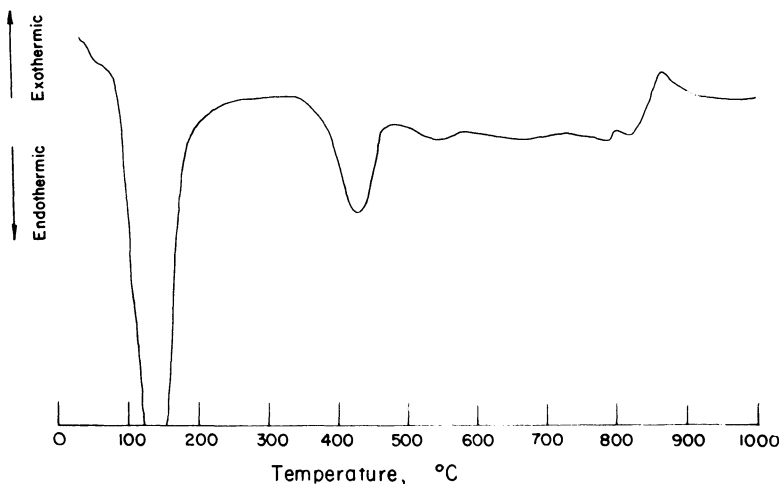


Figure 2. Differential thermal analysis curve for lime-bentonite after one year. Original bentonite endotherm was at 680°C.

SINGLE CRYSTAL DATA

The aged lime-bentonite was examined under binocular and petrographic microscopes for new crystals. To facilitate picking, a representative sample was removed, broken up by gentle agitation in distilled water, and filtered. Material passing the #40 sieve and retained on the #60 sieve was found to contain crystals of suitable size. Crystals were mounted individually on glass fibers with Canada Balsam, and a fiber was placed on the goniostat of the General Electric single crystal orienter. X-ray measurements were made using both molybdenum and copper radiation. Diffraction intensities and crystal orientations were recorded, and by means of the orientations and d-spacings the reciprocal lattice was constructed and Miller indices assigned. The unit cell dimensions were calculated from these data (table I) and from the angular coordinates for the various orientations using the procedures outlined by Buerger (10). The unit cell parameters are shown in Fig. 3.

Table I. Partial Single Crystal Diffraction Data, (Mo & Cu Radiation)

Goniostat		Triclinic hkl	Goniostat		Triclinic hkl
d	I		d	I	
11.857	W	010	1.98	VS	400
7.939	W	100	1.97	M	060
7.357		001	1.91	S	204
6.72	S	110	1.80	M	260
6.68	M	101	1.76	W	260
6.53	S	110	1.74	S	350
5.93	S	020	1.68	S	501
4.07	M	031	1.68	W	440
4.01	M	012	1.66	M	404
3.97	VS	200	1.65	M	073
3.92	W	201	1.62	W	440
3.85	VW	102	1.61	W	503
3.64	VS	130	1.51	S	305
3.53	VS	130	1.41	VS	602
3.38	VS	220	1.35	W	550
3.33	VS	202	1.34	W	093
3.25	VS	220	1.32	M	505
2.96	S	040	1.30	W	550
2.81	S	301	1.29	S	620
2.60	S	310	1.28	M	620
2.57	VS	103	1.28	S	206
2.56	M	310	1.18	S	701
2.35	VS	240	1.10	M	606
2.25	M	330	1.03	W	0.10.6
2.23	M	401	1.01	S	804
2.21	M	303	0.992	W	800
2.17	W	330	0.918	W	806
2.08	VS	402	0.843	W	10.0.2
2.06	M	053			

Optical properties were measured with a petrographic microscope equipped with a universal stage. The mineral is biaxial negative, the angle between the optic axes being about 71° . Additional work is needed to determine refractive indices.

REACTION PRODUCT POWDER DATA

Due to the difficulty of obtaining all possible reflections using the single crystal orienter, several of the product crystals taken from the mixture were crushed for powder photographs. A suitable mount was found to be a solid glass fiber coated with rubber cement. Rotating powder photographs were taken with a small diameter Debye-Scherrer camera using chromium radiation to afford maximum separation of lines. Strong intensity lines and those with longest d-spacings are listed in Table II.

The reaction product giving a line at 9.93 Å in figure 1 has not yet been isolated. The composition of the 7.93 Å crystals is not known and can not readily be determined by conventional wet chemical methods; the problem will be approached by use of an electron microprobe.

CONCLUSION

X-ray diffraction studies of a slowly cured mixture of dolo-

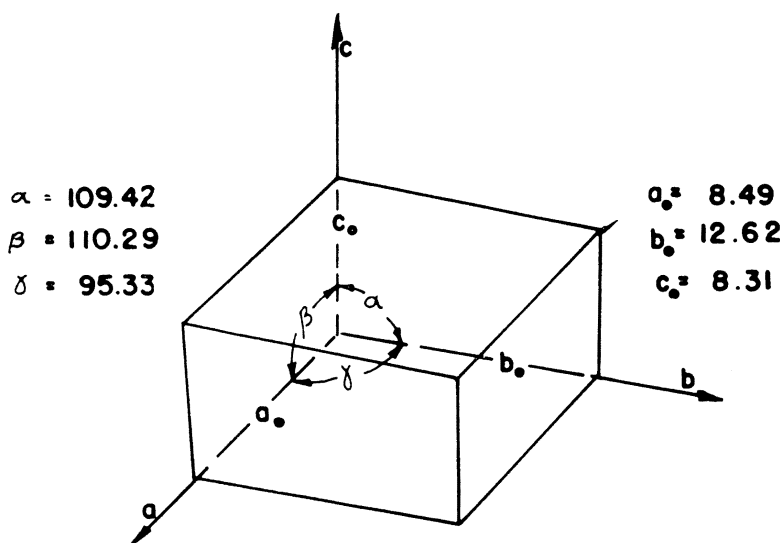


Table II. Selected Powder Diffraction Data (tentative)

hkl	calc. d, Å	obs. d, Å	Intensity
100	7.93	7.9	1, var.
111	6.74	6.70	4
110	6.67	6.70	4
a	...	6.26	(2)
b	...	4.25	(8)
210	3.79	3.76	5
210	3.73	3.76	5
c	...	3.44	(4)
220	3.26	3.27	3
021	3.23	3.22	10
040	2.96	2.97	4
211	2.90	2.90	3
131	2.77	2.76	2
022, 113, 141	2.75	2.76	2
310	2.59	2.56	3
240	2.40	2.38b	2
113	2.37	2.38b	2
103	2.15	2.16	3
204	1.93	1.92	3
260	1.79	1.80	8

a, b, c Probable impurities.

mitic monohydrate lime and bentonite show new pozzolanic reaction products, one of which was isolated and characterized by single crystal X-ray and optical methods. X-ray and differential thermal analysis of the reacted mixture also indicates considerable alteration of the clay mineral.

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Radiochemistry and Removal Characteristics of Radium Isotopes in Iowa Well Waters

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Abstract. Significant concentrations of radium —226, a naturally occurring isotope which has no relationship to fallout, have been detected in a number of deep wells in Iowa. Wells that have significant radium concentrations are located in smaller communities mostly in southeastern part of the State. Several of the towns have municipal zeolite softening processes which remove radium down to low levels. In some cases where the raw well water shows relatively high concentrations, zeolite softened water distributed to the public has had approximately 90 percent of the radium removed. Wells tested so far show that the average radium values are in most instances within the range specified by the Federal Radiation Council.

Deep well waters from the Jordan aquifer in Southeastern Iowa yield levels of radium 226 often exceeding the present radiation protection guide recommended by the Federal Radiation Council in their Staff Report #2. The State Hygienic Laboratory in cooperation with the Iowa Geological Survey and Argonne National Laboratories has been investigating this situation in an attempt to delineate the various geologic, radiochemical and epidemiological factors involved.

Radium 226 and isotopes Ra²²⁸ and Ra²²⁴ have been existing in our Jordan aquifer for millions of years and have no relation

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